Activation of Co Fischer-Tropsch Catalyst: Exploring Co Valence State under Different Reduction Conditions Using STEM-EELS

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Cobalt (Co) is rarely available as a pure reduced metal for industrial Fischer-Tropsch Synthesis (FTS) due to its tendency to oxidise rapidly [1]. As a result, the production of active metallic Co is typically achieved through the reduction of spinel cobalt oxide (Co_3O_4) in the FTS catalytic reactor prior to the synthesis. Occasionally, depending on the reactor temperature and the composition of the reducing atmosphere, Co_3O_4 does not fully reduce to active metallic Co, resulting in a catalyst with mixed Co valence states, crystallographic phases and surface terminations [2]. In this case, the activity of the catalyst is reduced while the selectivity towards methane is increased [3]. Electron energy loss spectroscopy (EELS) can be used to obtain information about the valence states of reduced Co from the Co-$L_{3,2}$ edge fine structure, and the oxygen K edge [4]. Specifically the Co valence state varies according to the L_3/L_2 peak intensity ratio, the $L_{3,2}$ peak-to-peak energy resolution, and the onset energy loss of the L_3 peak and O-K pre-peak [5,6]. Hence, these parameters can be used to measure quantitatively the oxidation state of the catalyst after reduction. Herein, we investigate the *ex-situ* reduction of Co_3O_4 nanoparticles supported on hollow carbon spheres as the catalyst precursor for the FTS under H_2 gas and syngas at 350 °C. The reduced Co catalyst was studied in an aberration corrected analytical scanning transmission electron microscope (JEOL ARM200F) fitted with a Gatan GIF Quantum 965 ER, at 200 kV using a semi-convergence angle of 14 mrad for simultaneous acquisition of both EELS and ADF signals. Figure 1 shows the EELS spectra and the associated O-K edge (red) and Co-$L_{3,2}$ edge (green) elemental maps of the pristine, 350 °C hydrogen reduced, and 350 °C syngas reduced Co catalyst. These results suggest that syngas achieves a higher degree of reduction than H_2 gas at 350 °C. This is reflected in Figure 1 (a) by the shift of the Co-L_3 edge to lower energy losses with decreasing Co valence state and the intensity of the O-K edge pre-peak (peak 'α' in Figure 1(a)), which decreases with decreasing Co valence state. Furthermore, a higher degree of reduction is indicated on the elemental maps by the intense Co-$L_{3,2}$ edge signal across the syngas reduced catalyst particle (Figure 1(d)) compared to the hydrogen reduced catalyst particle (Figure 1(c)). In this contribution we will discuss the most effective routes for the activation of cobalt FTS catalysts where maximum reduction is achieved.

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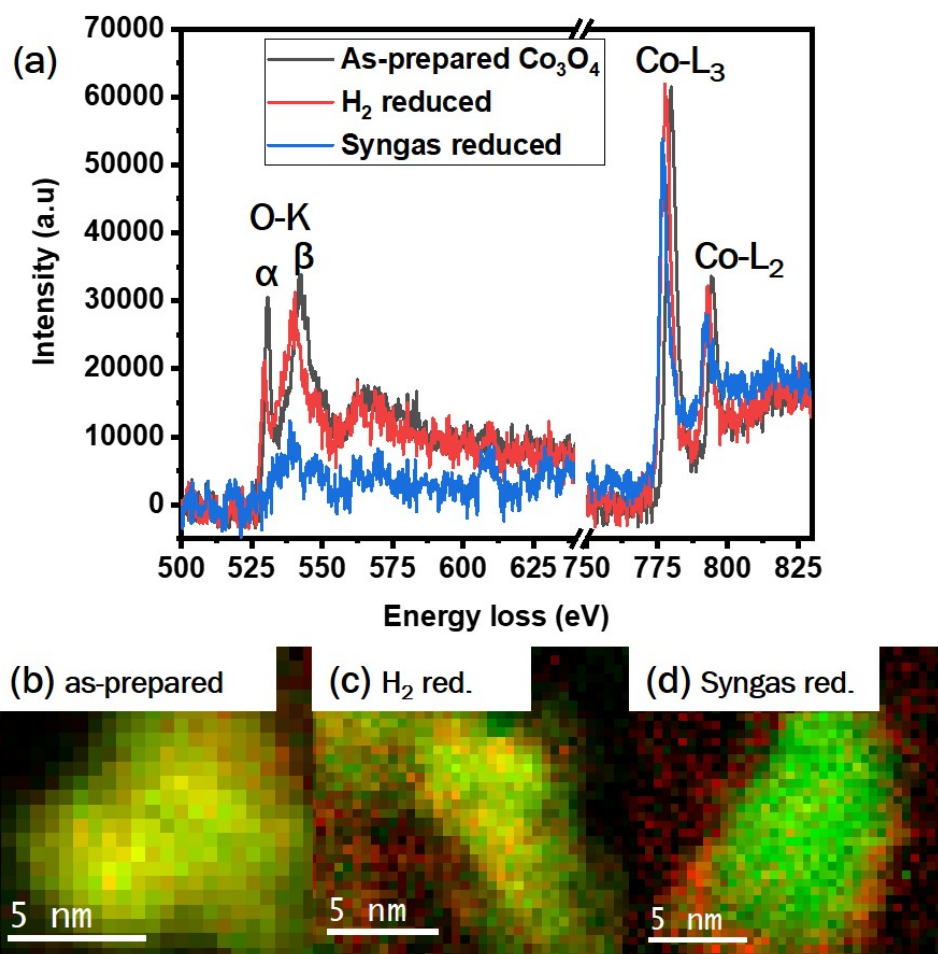
Figure 1. (a) EELS spectra of as-prepared CO_3O_4 (black), 350 °C 10% (v/v) hydrogen reduced (red), and 350 °C syngas (1:2 CO:H2) reduced catalyst (blue). (b), (c), and (d) are EELS elemental maps of as-prepared, hydrogen reduced, and syngas reduced Co catalyst, respectively. Red shows the O-K edge signal and green the $Co-L_{3,2}$ edge signal.